Perspective Report Series 2

LIQUID CRYSTALS

S. CHANDRASEKHAR

Raman Research Institute,
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1. Introduction

In an article entitled *Unity of Concepts in the Structure of Matter* published three years ago, John Bardeen[1] wrote : "In this age of increasing specialization it is comforting to realize that basic physical concepts apply to a wide range of seemingly diverse problems. Progress made in understanding one area may often be applied in many other fields. This is true not only for various fields of materials science but for the structure of matter in general. As examples we illustrate how concepts developed to understand magnetism, superfluid helium, and superconductivity have been extended and applied to such diverse fields as nuclear matter, weak and electromagnetic interactions, quark structure of the particles of high energy physics, and phases of liquid crystals."

"Theoretical methods used in quantum field theory and in many-body problems of condensed-matter theory have much in common. For example, Greens function methods, Feynman diagrams, and renormalization group methods introduced for quantum electrodynamics have also been used in many problems in condensed-matter physics. The concept of spontaneously broken symmetry and associated phase transitions derived for condensed-matter are now being widely used for problems of high energy physics."

A large part of the present paper will be devoted to demonstrating some aspects of Bardeen's predication by choosing a few examples from recent work on liquid crystals carried out at Bangalore and elsewhere. The topics that we shall discuss are :

i) The first experimental determination of the decrease in the smectic A—nematic transition point brought about by a twist deformation, an effect which is the analogue of the influence of a magnetic field on the superconductor-normal metal transition.

ii) The analogy between the hydrodynamics of cholesteric liquid crystals and superfluid hydrodynamics, and some of its consequences, e.g., the possibility of a temperature wave attending second sound in the cholesteric phase.

iii) The core structure of a smectic C disclination and its similarity to a quantized vortex filament in a superfluid or a magnetic fluxoid in a type II superconductor.

iv) The nematic-smectic A-smectic C multicritical point.

The concluding part of the paper will deal with a brief summary of recent progress in liquid crystals of disc-like molecules.

Some basic knowledge of the structure and physical properties of thermotropic liquid crystals will be assumed. [For an introduction to liquid crystals of rod-like molecules see Chandrasekhar[2]; and of disc-like molecules, Chandrasekhar[3,4].] The discussion will be mostly qualitative, with emphasis on the physical principles rather than the detailed mathematical theory.

2. The Effect of a Twist Deformation on the Smectic A—Nematic Transition Point

Recognizing the analogy between the smectic A phase and the superconductor, de Gennes[5] predicted that a twist or bend distortion should depress the smectic A-nematic transition point, T_{AN}, relative to the curvature free sample. The nature of the phase diagram depends on whether the material is of type I or type II, i.e., on whether the Ginzburg-Landau parameter, λ/ξ, is less or greater than $1/\sqrt{2}$, where λ is the penetration depth for a twist or bend deformation and ξ the coherence length. However, compounds which exhibit a second order or nearly second order A-N transition are expected to be of type I[6]. The threshold curve is then given by

$$\frac{\alpha^2}{2\beta} = \frac{1}{2} k_{ii} (\vec{\nabla} \times \mathbf{n})^2, \qquad i = 2 \text{ or } 3$$

where α and $\frac{1}{2}\beta$ are the usual coefficients of the second and fourth order terms in the Ginzburg-Landau free energy expression, and k_{22} and k_{33} the Frank constants for twist and bend respectively. If, for the sake of argument, we assume a mean field approximation (though it is known not to be valid for this transition) we may put $\alpha = \alpha_0 (T - T^*)$, where T^* is the second order A-N transition point. The decrease in the transition temperature due to a twist or bend distortion is then easily shown to be

$$T^* - T_{AN} = \frac{1}{\alpha_0} \left(\frac{k_{ii}}{\beta} \right)^{1/2} \nabla \times \mathbf{n}$$

Moreover, the transition becomes first order, the order parameter at T_{AN} being given by

$$|\Psi|^2_{T=T_{AN}} = \frac{\alpha_0 (T^* - T_{AN})}{\beta} .$$

The origin of this effect is readily understood. The nematic has curvature elasticity, i.e., a very weak elasticity associated with the orientational deformation of the director. The free energy density of elastic deformation

$$F = \tfrac{1}{2} k_{11} (\vec{\nabla} \cdot \mathbf{n})^2 + \tfrac{1}{2} k_{22} (\mathbf{n} \cdot \vec{\nabla} \times \mathbf{n})^2 + \tfrac{1}{2} k_{33} (\mathbf{n} \times \vec{\nabla} \times \mathbf{n})^2,$$

where k_{11}, k_{22} and k_{33} are the Frank elastic constants for splay, twist and bend respectively. Smectic A, on the other hand, is a lamellar structure composed of liquid-like layers with the rod-like molecules upright, on the average, in each layer. The layers themselves are very flexible, whereas a compression of the layers require enormous energy by comparison. Now, both the twist and bend deformations of the director involve a change in the layer spacing, and are therefore expelled by the smectic A phase; in other words, $(\vec{\nabla} \times \mathbf{n}) = 0$, which is the analogue of the *Meissner effect* in superconductors, **n** playing the role of the magnetic vector potential.

The influence of a magnetic field on the superconductor-normal metal transition has, of course, been very well studied. Typical curves are shown in Fig. 1. Surprisingly, although it is now over 10 years since de Gennes predicted a similar type of diagram for T_{AN} versus $|\vec{\nabla} \times \mathbf{n}|$, there have been (until recently) only two experiments that have taken note of this effect to give a qualitative explanation of some observations. The first was by Cladis and Torza[8] who observed a 'striped' texture when a sample of CBOOA (N-p-cyanobenzylidene-p′-octyloxyaniline, which has a nearly second order A–N transition) with a strong bend distortion was cooled to T_{AN}. This they interpreted as the formation of an 'intermediate' state with the A and N phases co-existing. Subsequently, similar observations were reported by Hinov[9] on CBOOA with a bend induced by an electric field.

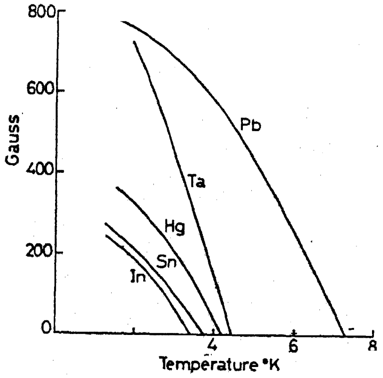


FIG. 1. Variation of the superconductor-normal metal transition temperature versus the applied magnetic field. (From Roberts and Miller[7]).

The first quantitative measurements of the dependence of T_{AN} on $|\vec{\nabla} \times \mathbf{n}|$ were made only recently by Madhusudana and Srikanta[10,11]. They used a twisted nematic cell in the form of very low angled wedge (Fig. 2). The twist angle was about 75°, the twist per unit length, of course, varying along the length of the wedge. The cell thickness at different points was first determined accurately by the optical interferometric technique, and as the twisted nematic sample was cooled the temperatures at which the smectic A phase just made its appearance at these points were noted (to ± 10 millidegrees). Madhusudana and Srikanta investigated the phase diagrams of two compounds, CBOOA[10] and 8 OCB[11] (*p-n*-octyloxy-*p'*-cyanobiphenyl which shows a weak first order A-N transition even in the absence of a curvature distortion), and both compounds showed the expected trend. The results for CBOOA are presented in Fig. 3. It is remarkable that such an extremely weak type of elastic deformation should produce a detectable change in the transition temperature.

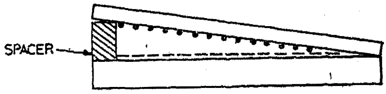


FIG. 2. Schematic diagram of the wedge-shaped twisted nematic cell used for the determination of the dependence of the smectic A-nematic transition point on $|\vec{\nabla} \times \mathbf{n}|$. Wedge angle ≃ 0.001 radian. The director is anchored parallel to the plane of the paper at the bottom surface and almost, but not exactly, perpendicular to the plane of the paper at the top.

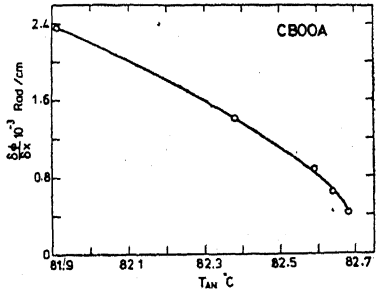


FIG. 3. Experimental variation of the smectic A-nematic transition temperature (T_{AN}) with the twist per unit length ($\delta\varphi/\delta x$) for CBOOA. (Madhusudana and Srikanta[10]).

There are other aspects of this analogy. For example, there should be pretransition anomalies : the coherence length, which is a measure of the size of the smectic-like clusters in the nematic phase, and the related properties should diverge as the temperature approaches T_{AN}. This has been extensively studied by a variety of techniques. The critical exponents associated with this divergence have been the subject of much discussion, and unfortunately the experimental values reported by the different investigators are not in agreement (for a summary of the results up to 1978, see Chandrasekhar and Madhusudana[12]). However, the latest position, which is based on the very precise studies by the MIT group, is that it is definitely not mean field, but closer to the ^{4}He analogy, though there are significant departures from this analogy which still remain to be understood from the theoretical point of view. (For excellent up-to-date accounts of the current situation see Litster *et al.*[13] and Lubensky[14].)

3. Thermomechanical Effects in Cholesteric Liquid Crystals

Smectic A has a complex order parameter, $\psi = |\psi| \exp(i\varphi)$, where $|\psi|$ is the amplitude of the one dimensional density wave and φ a phase factor that determines the positions of the layers[5,15]. In effect, the layer displacements are uncoupled with the density. There are two propagating acoustic modes : one is the usual longitudinal (or compressional) wave, and the other associated with oscillations in the layer spacing without appreciable density changes (i.e., oscillations in the phase of the complex order parameter) and may be compared with the phonon branch in superfluids known as *second sound.* The velocity of second sound in smectic A is determined by the elastic modulus for the compression of the layers.

For long wavelength fluctuations, for which the distortions vary smoothly and slowly over several pitches, the cholesteric may also be looked upon as a layered structure, rather like smectic A. One can then employ a 'coarse-grained' approximation[16] and express the modulus for the layer compressibility (B) in terms of the Frank constant (k_{22})

$$B = k_{22}q_0^2, \qquad \ldots(1)$$

where $q_0 = 2\pi/P_0$, P_0 being the pitch of the undistorted cholesteric. Thus second sound may be expected to occur in cholesterics also, as was first discussed by Lubensky[17], but there is an additional effect which has recently been investigated by Ranganath[18], viz., that *the phase fluctuations should be accompanied by temperature fluctuations as well,* bringing the analogy with superfluids even closer.

To appreciate the significance of this effect, we go back to an observation reported by Lehmann[19] very soon after the discovery of liquid crystals. Lehmann noted that when the cholesteric material was taken between glass plates and heated from below the different droplets appeared to be rotating violently, but on closer examination he concluded that it was not the droplets themselves but the structure that was rotating. Leslie[20,21] pointed out that the absence of a plane of symmetry in the cholesteric structure automatically implies that there can be a coupling between thermal and mechanical effects. Specifically, his equations showed that when a thermal gradient is imposed along the helical (z) axis, then the director (which is in the x-y plane) should experience a torque about z; or, conversely, a rotational motion of the director about the z axis should, in principle, generate heat flow along z. It is seen at once that this explains

Lehmann's rotation phenomenon and, in fact, Leslie[20] derived an expression for the angular velocity of the director in the presence of a thermal gradient along the helical axis. (For a concise account of Leslie's theory and its application see Chapter 4 of Chandrasekhar[2].)

Now, a compression of the cholesteric layers (which, as we have seen, determines the second sound velocity) means a change of pitch or, equivalently, a change in the twist per unit length of the director. It follows therefore that fluctuations in the layer spacing should be accompanied by orientational fluctuations of the director about the helical axis, and this in turn, because of the thermomechanical coupling, should result in temperature fluctuations.

Suppose that the distortions are of small amplitude and that they vary slowly and smoothly over several pitches. Under these circumstances, one may ignore the director inertia and average out all the high frequency components. Suppose also that the distortions are such that the tilt of the director away from the plane of the local layer is small. Then taking the cholesteric axis to be along the x_3 direction (z-axis), Leslie's equations simplify to[18]

$$\frac{1}{\rho}\frac{\partial \rho}{\partial t} + v_{i,i} = 0$$

$$\rho \frac{\partial v_i}{\partial t} = -P_{,i} + \delta_{i3} g + t'_{ij,j}$$

$$\frac{\partial u}{\partial t} - v_3 = -\left(\frac{1}{\lambda_1 q_0^2}\right) g - \left(\frac{\lambda_3}{\lambda_1 q_0}\right) T_{,3}$$

$$\frac{dQ}{dt} = K_{\parallel}\, T_{,33} + K_{\perp}\,(T_{,11} + T_{,22}) - \lambda_3 q_0 \left(\frac{\partial u}{\partial t} - v_3\right)$$

$$g = k_{22}\, q_0^2\, u_{,33}.$$

Here, we employ the cartesian tensor notation, repeated tensor indices being subject to the usual summation convention, the comma denoting partial differentiation with respect to spatial coordinates

$$\left(\text{i.e., } v_{i,i} = \frac{\partial v_i}{\partial x_i}\,;\quad T_{,33} = \frac{\partial^2 T}{\partial x_3^2}\,,\ \text{etc.}\right);$$

ρ is the density, v_i the velocity, P the pressure, t'_{ij} the hydrodynamic stress tensor, uq_0 the change in the local orientation of the director in its own plane, λ_1 the twist viscosity coefficient, λ_3 the thermomechanical coefficient, Q the heat supply per unit volume and $K_{\parallel}$ and $K_{\perp}$ are the thermal conductivity coefficients along and perpendicular to the twist axis. We have also assumed Onsager's reciprocal relations for irreversible processes.

From these equations, it is easily shown that there are two propagating modes. One is the usual longitudinal wave, whose velocity is practically independent of the direction of propagation and is determined by the volume compressibility, and the other is the second sound whose velocity

$$c_2 = (B/\rho)^{1/2} \sin\theta \cos\theta \qquad \ldots(2)$$

where B is given by eqn. (1) and θ is the angle between the wave-vector and the z axis. Eqn. (2) was first derived by de Gennes[16] for smectic A, and by Lubensky[17] for the cholesteric, but, additionally, we now have temperature fluctuations associated with second sound. The ratio of the amplitude of the temperature wave to that of the phase wave is[18]

$$f = -k_{22}\, q_0/\lambda_3.$$

For positive λ_3 the temperature wave is a propagating mode, while for negative λ_3 it is not.

Similarly, Ranganath[18] has shown that in the case of steady flow, neglecting viscous effects and permeation,

$$\partial P/\partial T = -\lambda_3\, q_0,$$

which is comparable with London's equation for the fountain effect in superfluids, and also that there can be an extra thermal conductivity analogous to thermal superconductivity.

However, we shall not discuss these effects in any further detail because the experimental situation is not at all clear. As far as I am aware, no one has succeeded in reproducing Lehmann's observations. We, therefore, decided that it might be worthwhile devising some experiments which should enable a determination of the magnitude and sign of the thermomechanical effect, if it exists. With this in view, we have recently proposed two experimental geometries[22].

In the first geometry, the sample is taken in a capillary with the cholesteric axis along the capillary axis. The inside surface of the capillary is supposed to be treated so that the cholesteric layers are firmly anchored and prevented from moving, at least at low shear rates[23,24]. A temperature gradient along the capillary axis should then result in a helical motion of the director and give rise to fluid flow. The quantity of fluid flowing per second is given by[22]

$$Q = \frac{\pi R^2}{q_0} \frac{\lambda_3}{\lambda_1} T_{,z},$$

where R is the radius of the capillary and λ_1 is the usual twist viscosity coefficient and $T_{,z}$ the temperature gradient. Conversely, as shown by Prost[25], if flow is induced by a weak pressure gradient, a temperature difference should develop across the ends of the capillary. Either of these measurements should yield λ_3 in sign and magnitude.

In the second geometry[22], a temperature gradient is imposed at right angles to the cholesteric axis. The theory shows that the uniaxial symmetry of the structure will then be destroyed. A measurement of the birefringence for light propagating along z provides an estimate of the thermomechanical coefficients.

The experiments have yet to be conducted, but if it does turn out that the thermomechanical effect is of measurable magnitude, then the analogies with superfluid hydrodynamics will become more meaningful, and this should certainly open up interesting areas for further study.

4. The Core Structure of a Smectic C Disclination

Smectic C is a tilted form of smectic A, i.e., the director is inclined with respect to the layer normal. (As emphasized by Frank[26], this definition is not strictly correct, but is adequate for the present discussion). The smectic C-smectic A transition has been established to be continuous for a number of compounds (see, for example, Meichle and Garland[27]) and optical and x-ray studies have shown that the tilt angle ω (measured with respect to the layer normal or the z-axis) decreases gradually as the temperature approaches the transition and becomes zero at T_{CA}. The order parameter of smectic C is a complex quantity, $\psi = \omega \exp(i\varphi)$, where φ is the azimuthal angle of the projection of the director on a plane parallel to the layers (the xy-plane)[6]; ω is directly coupled with the layer thickness whereas φ is not. Near T_{CA} (i.e., for small ω) the free energy density in the C phase may be written as[6]

$$F = \alpha\omega^2 + \tfrac{1}{2}\beta\omega^4 + \tfrac{1}{2}k_{11}\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right)^2$$

$$+ \tfrac{1}{2}k_{22}\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x}\right)^2 + \tfrac{1}{2}k_{33}\left(\frac{\partial n_x}{\partial_z} + \frac{\partial n_y}{\partial z}\right)^2 \quad \ldots(3)$$

where $\alpha = \alpha_0 (T - T_{CA})$ in the mean field approximation, $n_x = \omega \cos\varphi$, $n_y = \omega \sin\varphi$, $n_z \simeq 1$. The contributions due to the compressibility of the layers are neglected. Making the simplifying assumption that $k_{11} = k_{22} = k_{33} = k$ and that ω and φ are independent of z the free energy leads to (Ranganath[28]),

$$\tfrac{1}{2}k\,[\nabla^2\omega - \omega(\nabla\varphi)^2] - \alpha\omega - \beta\omega^3 = 0 \quad \ldots(4)$$

and

$$2\omega(\nabla\omega . \nabla\varphi) + \omega^2(\nabla^2\varphi) = 0 \quad \ldots(5)$$

The solutions of (5) are

$$\varphi = \pm s\theta, \quad \ldots(6)$$

where s is an integer and $\theta = \tan^{-1} y/x$. Eqn. (6) describes the in-plane distortions of the director around the line singularities or disclinations which can be observed in the optical schlieren textures exhibited by smectic C. (They are exactly equivalent to the defects of integral strength in the nematic.) From eqn. (4) it is seen that these distortions should alter the tilt angle as well, and this enables one to investigate the core structure. The variation of ω with distance r from the centre of the singularity (for $|s| = 1$) obeys the differential equation (Ranganath[28])

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial f}{\partial \xi}\right)-\frac{f}{\xi^2}+f(1-f^2)=0 \qquad \ldots(7)$$

where $\xi = r/\xi_0$, ξ_0 is the coherence length $= (-k/2\alpha)^{1/2}$, $f = \omega/\omega_0$ and ω_0 is the tilt angle at $r \to \infty$. Eqn. (7) is precisely of the same form as the Ginzburg-Pitaevskii equation for the vortex filament in a superfluid or a magnetic fluxoid in a type II superconductor (see Lifshitz and Pitaevskii[29], Grassie[30]). The tilt angle drops to zero at the centre of the singularity (Fig. 4), and this is in conformity with optical observations[31].

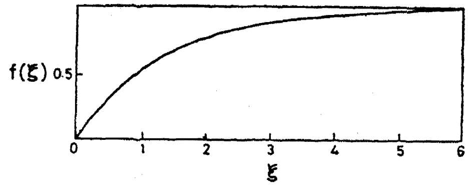


FIG. 4. Variation of the superfluid order parameter with distance from the centre of a quantized vortex filament as given by the Ginzburg-Pitaevskii equation (From Lifshitz and Pitaevskii[29]). The same curve describes the variation of the tilt angle in the core region of a smectic C disclination (Ranganath[28]).

5. The Nematic-Smectic A-Smectic C Multicritical Point

The nematic-smectic A-smectic C (NAC) point was predicted theoretically by Chen and Lubensky[32] as a possible realization of a *Lifshitz point* in a liquid crystalline system. The Lifshitz point itself was proposed earlier by Hornreich, Luban and Shtrikman,[33,34] who had in mind, as an example, the meeting point of the para-, ferro- and helicoidal magnetic phases in the temperature (T) *vs.* pressure (P) or concentration (X) diagram.

The first observations of the NAC point were made by Johnson *et al.*[35] and independently by Sigaud *et al.*[36] in the T-X diagrams of binary systems. Johnson *et al.*[35] who studied the $7\bar{S}5/8\bar{S}5$ (heptyl/octyl-oxy-p'-pentylphenylthiol benzoate) mixture, also reported accurate calorimetric measurements and established the following facts : the NA transition is throughout continuous, the AC transition is also throughout continuous, whereas the NC transition is weakly first order away from the NAC point but becomes continuous very close to and at the NAC point itself.

Thus the NAC point is a multicritical point at which the three phases become indistinguishable.

Safinya *et al.*[37] carried out a high-resolution study of the x-ray diffuse scattering arising from the smectic-like fluctuations in the nematic phase of the $\bar{7}$S5/$\bar{8}$S5 system. They found that close to the NC line the critical fluctuations are smectic C-like, but away from it the fluctuations become smectic A-like. However, the q-dependence of the intensity of scattering in the vicinity of the NAC point did not quite agree with the Chen-Lubensky mean field model, which predicts a $q_{\perp}^{-4}$ variation. (According to Safinya *et al.*[37] another model for NAC point proposed by Chu and McMillan[38] was found to be unsatisfactory in explaining these experimental results.)

More recently, Brisbin *et al.*[39] have investigated four other binary systems. They have found that despite differences in the global features, the topology of the phase diagrams around the NAC point itself is strikingly similar in all cases, so much so that they have suggested that the topology should be universal for this multicritical point. Their phase diagrams are reproduced in Fig. 5.

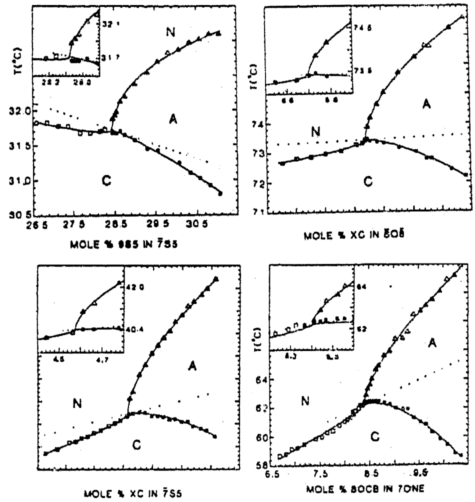
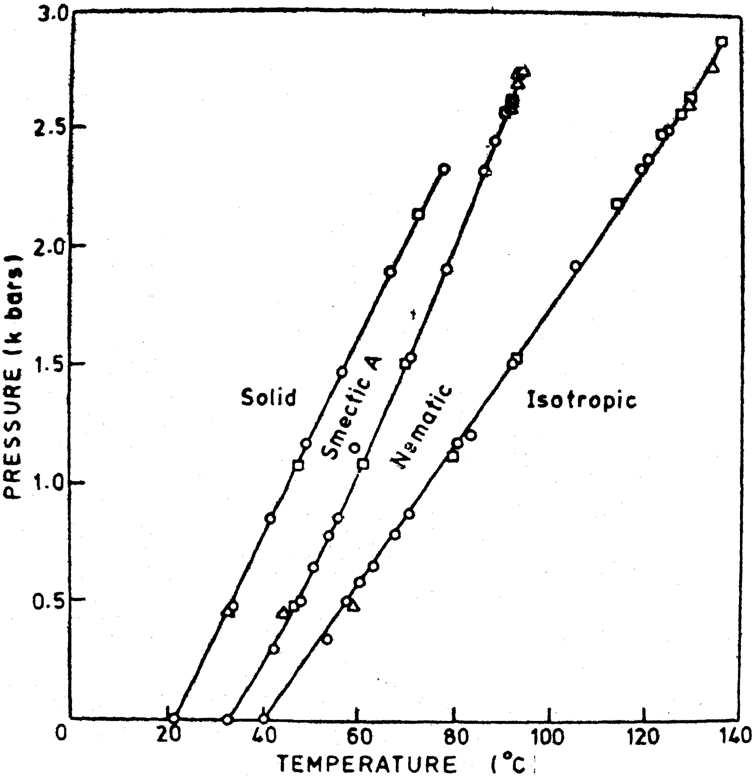


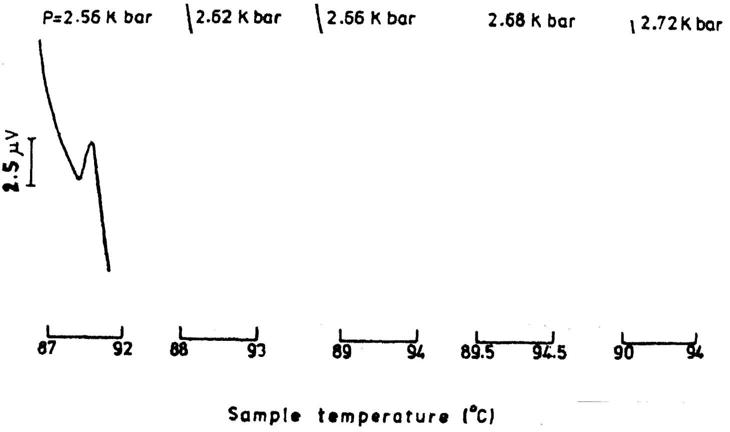
FIG. 5. Temperature-concentration diagrams for four binary liquid crystal systems in the vicinity of the nematic-smectic A-smectic C multicritical point (Brisbin *et al.*[39]).

Since 1973, high pressure experiments have been going on in our laboratory and these have been extremely fruitful in that they have led to the discovery of a variety of new phenomena of fundamental significance, as for example, pressure induced liquid crystallinity in certain materials, suppression of liquid crystalline phases in certain others, triple points, tricritical points, reentrant behaviour, etc. (see review by Chandrasekhar and Shashidhar[40]). An example of tricritical behaviour in the P-T diagram of a pure compound, observed by Shashidhar and Venkatesh[41], is presented in Fig. 6. Of late, Shashidhar and co-workers have been exploring the possibility of observing an NAC in a single component liquid crystalline system. The compound '50.6' [N-(4-*n*-pentyloxybenzylidene)-4′-*n*-hexylaniline] appeared to be promising in that the temperature range of the smectic A phase decreased initially with increase of pressure, but above about 4 kbar the NA and AC lines became nearly parallel (separated by just about 0.4°C) and the NAC point proved to be elusive.[42] Subsequently, Shashidhar *et al.*[43] discovered a new kind of multicritical point in the ompound DOBBCA [4(4-*n*-decyloxybenzoyloxy) benzylidene-4′- cyanoani-



(a)

FIG. 6. Tricritical behaviour of 8 CB (4′-*n*-octyl-4-cyanobiphenyl). (a) P–T diagram : circles, triangles and squares represent three independent sets of measurements.



(b)

FIG. 6. (b) Raw differential thermal analyses curves obtained for the smectic A-nematic transition at 5 different pressures illustrating the gradual diminution in the first order character of the transition as the pressure is increased beyond about 2.6 kbar. The tricritical point occurs at 2.68 ± 0.08 kbar and 92.5 ± 1.5°C. (Shashidhar and Venkatesh[41]).

line] which, at atmospheric pressure, shows the following sequence of transitions *on cooling* :

isotropic → nematic → sm A → sm C → reentrant nematic → crystal.

This compound shows a reentrant nematic-smectic C-smectic A (or RN-C-A) point. In order to get a better idea of the topology Shashidhar improved the accuracy of the pressure measurements (from ± 15 bar to ± 0.3 bar) and redetermined the *P-T* diagram[44]. The latest phase diagram for this compound is presented in Fig. 7. Independently, Sigaud *et al.*[45] observed a similar point, which they referred to as the 'inverted NAC point', in the *T-X* diagram of a binary system. Interestingly their diagram (reproduced in Fig. 8) is quite similar to that for DOBBCA; for example the RN-C and RN-A lines near the RN-C-A point are collinear in both cases. However more experiments are needed to draw definitive conclusions regarding the topology in the vicinity of this new multicritical point. Also it is of considerable importance to find a normal NAC point in a pure compound to verify that Johnson's conclusions have general validity. On the theoretical side, it is clear that these multicritical points are by no means fully explained, and that what is needed is a more complete analysis of the problem in terms of the renormalization group theory.

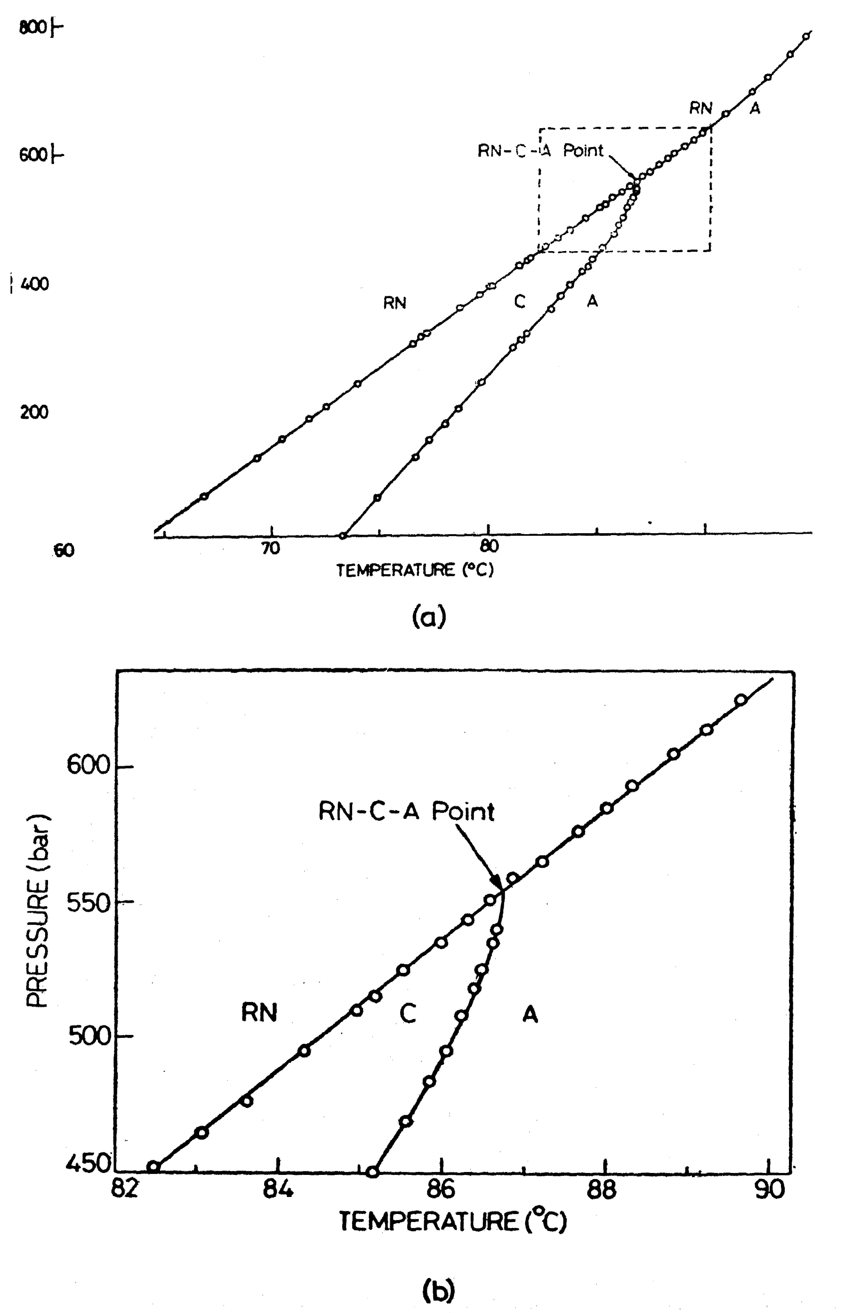


FIG. 7. (*a*) P–T diagram for DOBBCA showing a reentrant nematic-smectic C-smectic A multicritical point. (*b*) The portion of the diagram within the dashed lines in (*a*) drawn on an enlarged scale (Shashidhar *et al.*[44]).

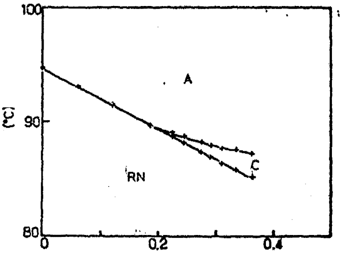


FIG. 8. Temperature-concentration diagram for a binary liquid crystal mixture of DOBBCA and 4-cyanobenzylidene-4′-(4″-decyloxybenzoyloxy) aniline showing a reentrant nematic-smectic C-smectic A multicritical point (Sigaud *et al.*[45]).

6. Liquid Crystals of Disc-like Molecules

We shall now turn our attention to liquid crystals of disc-like molecules. Following their discovery six years ago (Chandrasekhar *et al.*[46]), there has been a surge of activity in this field, and a large number of disc-like mesogens have been synthesized, some of which show a rich polymorphism comparable to that exhibited by systems of rod-like molecules. [For a more or less complete list of compounds studied to-date see Chandrasekhar[3]]. The liquid crystalline phases so far identified fall into two distinct categories : the columnar and the nematic. The columnar phase consists of discs stacked *aperiodically* in columns, the different columns constituting a two dimensional array, while the nematic phase is an orientationally ordered arrangement of discs without any long range translational order. A twisted nematic (or cholesteric) has also been identified, but a smectic type has not yet been found to occur.

The discovery of these phases has stimulated a number of theoretical studies, e.g., on the hydrodynamics of the columnar liquid crystal and the prediction of *two* second sound modes in this phase[47-49], on new types of defect structures[50-54], etc. Some of these studies have already been briefly outlined in a review article by the present writer (Chandrasekhar[3]) and therefore will not be discussed here. We shall merely refer to a few of the more recent advances in this field.

i) *Two-dimensional crystallography* : The columnar structure has translational periodicity in two dimensions but not in the third. The occurrence of a large variety of such structures in liquid crystals of disc-like molecules has paved the way for systematic x-ray analysis in terms of the 80 planar crystallographic space groups, which have so far remained more or less of purely theoretical interest. Outstanding work in this area has been done by Levelut[55], whose latest results are presented in Table I.

TABLE I : *Structures of some columnar phases* (*Levelut*[55])

Molecule		Space Group	Lattice parameters in Å	Temperature °C
Core	Chain (each molecule has six such chains)			
Benzene	C_7H_{15}—COO—	P 2_1/a	a = 31.2 b = 18.6	84
	C_6H_{13}—COO—	P 2_1/a	a = 28.5 b = 17.7	86
Triphenylene	C_5H_{11} O—	P 6 2/m 2/m	a = 18.95	≃ 80
	C_7H_{15} O—	P 6 2/m 2/m	a = 22.2	≃ 80
	C_8H_{17} O—	P 6 2/m 2/m	a = 23.3	≃ 80
	$C_{11}H_{23}$COO—	P 2_1/a	a = 44.9 b = 26.4	117
		P 6 2/m 2/m	a = 26.3	105
	C_7H_{15}COO—	P 2_1/a	a = 37.8 b = 22.2	100
	$C_{11}H_{23}$—O—φ —COO—	P 2_1/a	a = 51.8 b = 32.6	165
	C_6H_{13}—O—φ —COO—	C 2/m	a = 30.7 b = 28.4	185
Truxene	C_6H_{13} O—	P 6 2/m 2/m	a = 22.8	80
	$C_{10}H_{21}$ O—	P 6 2/m 2/m	a = 27.5	80
	$C_{14}H_{29}$ O—	P 6 2/m 2/m	a = 30.9	80
	C_9H_{19} COO—	P 6 2/m 2/m	a = 26.7	150
	$C_{13}H_{27}$ COO—	P 6 2/m 2/m	a = 30.5	150
	$C_{11}H_{23}$—O—φ —COO—	C 2/m	a = 44.1 b = 32.7	94
		C 2/m	a = 50.6 b = 33.8	180
	$C_{12}H_{25}$—O—φ —COO—	C 2/m	a = 44.6 b = 31.9	84
		C 2/m	a = 45.6 b = 35.3	180
Tribenzobenzofuran	$C_{13}H_{27}$—COO—	P 6 2/m 2/m	a = 30	160
		P 2_1/a	a = 49.2 b = 29.3	76
		P 1	a = 49.7 b = 28.0 γ = 97.5°	68
Anthraquinone		P 2_1/a	a = 34.8 b = 18.1	114
	C_7H_{15}COO	P 2/a	a = 34.9 b = 36	95

ii) *A mean field theory of the columnar-nematic transition* : This is essentially an extension of McMillan's theory of smectic A to a two-dimensionally periodic structure[4,47,56,57]. Calculations show that when the lattice is hexagonal, or departs from it only slightly, the transition from the columnar to the isotropic phase may take place either directly or *via* a nematic phase, depending on the model potential parameters α. Interpreting α to be a measure of the chain lengths as in McMillan's model, the theoretical phase diagram is in broad agreement with the experimental trends. As the asymmetry of the lattice is increased the theory predicts the occurrence of a smectic A phase as well[4,57]. The new smectic A phase is biaxial. As remarked earlier, a smectic phase of disc-like molecules is yet to be found.

iii) *Thermal fluctuations in the columnar liquid crystal* : As is well known from the classical work of Peierls and Landau, the 2D-lattice itself is an unstable system, but the weak Frank elasticity of the liquid-like columns stabilizes the long range two-dimensional order in the columnar phase. This fundamental question was investigated theoretically by us (Ranganath and Chandrasekhar[58], Chandrasekhar[4]) and independently and rather more thoroughly by Kammensky and Katz[59]. The remarkable result is obtained that the mean square fluctuation of the lattice as well as the Debye-Waller factor should show a dependence on the linear dimensions of the sample. For example, as far as the structure factor for the intensity of X-ray scattering is concerned, a narrow cylindrically shaped specimen with long columns may be expected to behave differently from a thin free film consisting of very short columns.

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